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By: Vijay K. Kapur, Leonard Nanis, and Angel Sanjurjo

Prepared for:

JET PROPULSION LABORATORY
California Institute of Technology
4800 Oak Grove Drive
Pasadena, CA 91103

Attention: Dr. Ralph Lutwack
Spacecraft Power Station

Contract No. 954471 under NAS 7-100
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Approved:



R. W. Bartlett, Director
Materials Research Center



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SUMMARY

Silicon obtained by the SiF_4 -Na reaction was analyzed by spark source mass spectrometry (SSMS). A partial listing of the results is given below. The concentration units in parentheses are ppm wt.

B(0.1), Al(0.8), Ga(0.06), P(0.2), F(0.1), Na(1.0), V(0.04), Mo(0.3), Ti(2.0), Zr(2.0), Mn(0.1), Ni(2.0), Zn(0.01), Cu(20.0), Cr(11.0), Fe(55.0)

An excellent starting material for silicon solar cells is obtained on the basis of the low levels of B, Al, Ga, P and As. The source of the Fe and Cr is suspected to be the stainless steel container for liquid sodium. An independent check for the phosphorus content in Sample 2-19 was made by a wet colorimetric method and was found to be 90 parts per billion (ppb), in reasonable agreement with the SSMS result of 200 ppb.

Silicon samples prepared from induction melted powder were evaluated for electrical properties using four-point probe conductivity and thermoelectric methods. The solid silicon in Sample 2-19 was found to be p-type and ranged in resistivity between 0.1 and 0.5 ohm cm.

A stainless steel reactor was designed and fabricated to perform the SiF_4 -Na reaction under P_{SiF_4} greater than 1 atmosphere. The amount of silicon produced was increased from 25 g per batch (in the glass reactor) to greater than 70 g per batch in the stainless steel reactor.

The study of the effects of reaction variables such as P_{SiF_4} and maximum temperature attained on the particle size of silicon powder showed that the silicon particle size tends to grow larger with increasing pressure of the SiF_4 gas in the reaction system.

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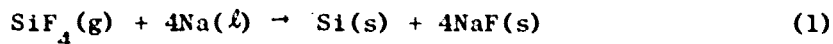
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INTRODUCTION

At the Materials Research Center of the SRI International, we have demonstrated¹ that silicon can be produced by the reduction of silicon tetrafluoride gas with liquid sodium according to the reaction



This reaction is exothermic and can be initiated by warming the reaction system to about 200°C.² A large amount of heat ($\Delta H^\circ_{500\text{ K}} \approx -164$ kcal/mole SiF_4) is liberated. Compounds appearing in the reaction products have been characterized.³ The separation of silicon from the reaction products by leaching out the sodium fluorides (NaF and Na_2SiF_6) has been studied in detail.⁴ The by-product Na_2SiF_6 , formed according to a side reaction



also has been studied in detail, and an understanding about its role in the overall process has been acquired.

A method has been reported for obtaining SiF_4 gas from commercial fluosilicic acid (H_2SiF_6) which is a waste by-product of the phosphate fertilizer industry.⁶ The impurity content in the SiF_4 gas thus prepared was found by mass spectrometric analysis⁷ to be much lower than that in commercial SiF_4 gas. In particular, the SO_2 content of the prepared SiF_4 was much lower.

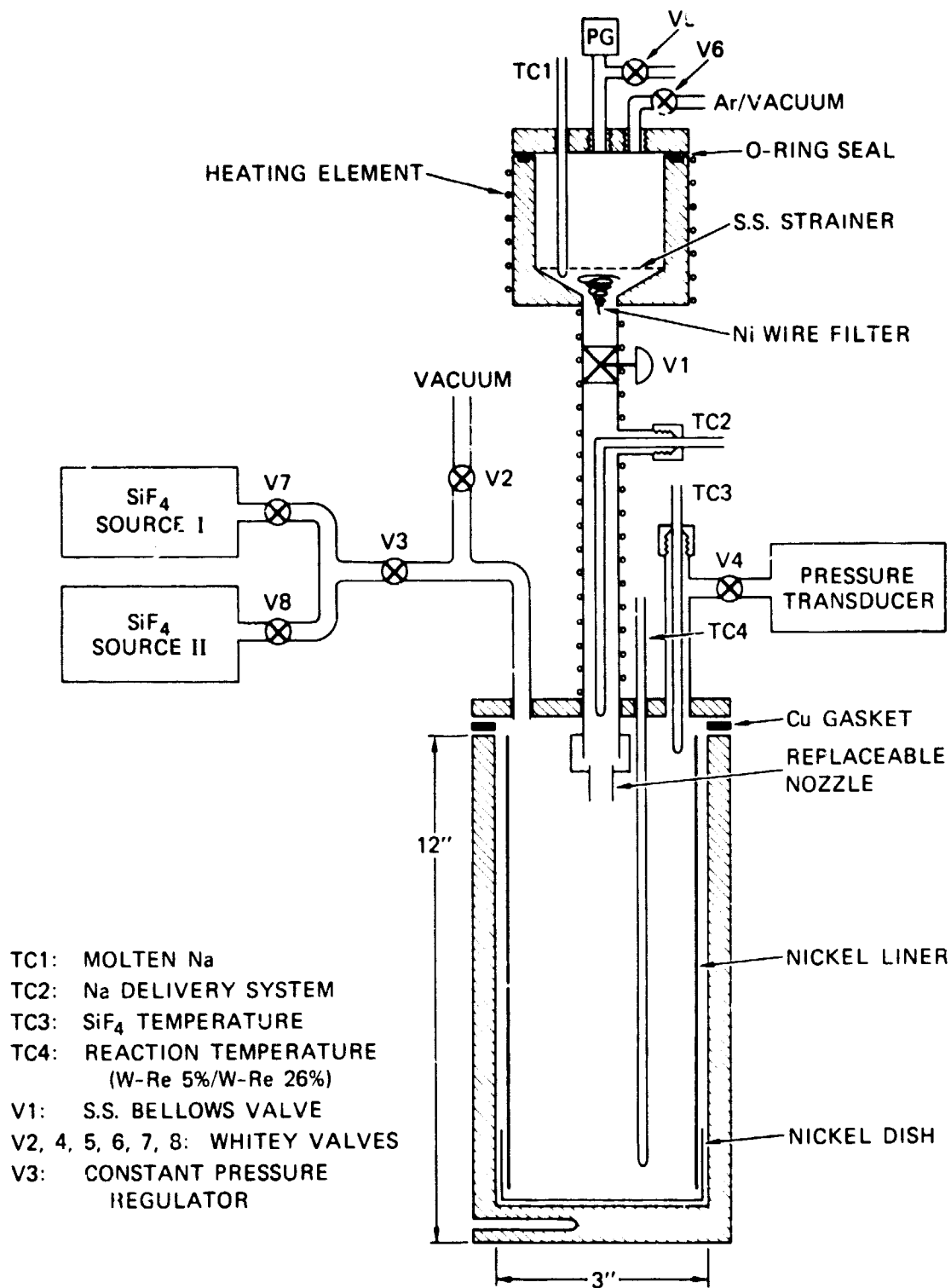
During this quarter, we have designed a stainless steel reactor for performing the SiF_4 -Na reaction with greater SiF_4 pressures. Experiments were performed to understand the effects of reaction parameters such as P_{SiF_4} and the maximum reaction temperature (T_{max}) on the morphology of the reaction products. Sieve analysis of the product silicon was used

to determine the particle size distribution and its correlation with the reaction variables. Scanning electron microscopy (SEM) was used to study product size and shape.

Our efforts this quarter also included the characterization of product silicon by its chemical analysis and by measuring its electrical properties. This report discusses these new developments in detail.

STAINLESS STEEL REACTOR

During the last quarter, we designed and fabricated a stainless steel reactor (see Figure 1) to replace the Pyrex glass reactor used previously. This reactor extends our capability to perform the SiF_4 -Na reactions with P_{SiF_4} greater than 1 atm. The reactor is 12 inches long and 3 inches in diameter and is constructed from a stainless steel (304) tube. The wall thickness of this tube is 1/16 inch. The tube is closed at one end with a 3/8-inch thick stainless steel plate and welded to a stainless steel vacuum flange with multiple entry ports. A stainless steel tube 3/8-inch OD welded in the center of the flange connects the reactor to a liquid sodium container (as described in Reference 5) through a bellows valve V_1 . A thermocouple TC2 placed inside this tube measures the temperature of the liquid sodium dropping into the reactor. To the lower end of this stainless steel tube, extending inside the reactor, various delivery nozzles can be attached for regulating the flow of liquid sodium into the reactor. The reactor is connected through a valve V_4 to a solid state pressure transducer and P_{SiF_4} inside the reactor is continuously recorded. A thermocouple TC3 in this port measures the temperature of the SiF_4 gas near the various entry ports. The reactor can be evacuated through a valve V_2 and it can also be connected to SiF_4 tanks through a constant pressure regulator V_5 . A high temperature thermocouple TC4 is inserted directly into the reactor to measure the reaction temperature. The inside of this stainless steel reactor is lined with a detachable nickel liner and a nickel dish, which prevents a direct contact between the reaction products and the stainless steel container. The reactor can be heated to initiate the reaction by the heating coils wound around its lower portion.



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FIGURE 1 STAINLESS STEEL REACTOR

With this reactor, we were able to increase the amount of silicon produced to 70 g per batch, compared with 25 to 30 g per batch in the glass reactor. Currently, this reactor is being used to study various ways of introducing liquid sodium into the reaction system.

EFFECTS OF PRESSURE (SiF_4) AND REACTION TEMPERATURE^{*}
ON THE MORPHOLOGY OF PRODUCT SILICON

Experience with the SiF_4 -Na reaction has shown that the maximum temperature attained in this exothermic reaction depends on the pressure of the SiF_4 gas in the system. The SiF_4 -Na reactions performed with $P_{\text{SiF}_4} \geq 1$ atm have been observed to proceed vigorously with reaction temperatures rising to above 1400°C . However, the SiF_4 -Na reactions performed with $P_{\text{SiF}_4} < 0.5$ atm have been observed to proceed mildly. The rate at which the reaction system is heated by the liberated reaction heat depends on the kinetics of the reaction. Increasing the P_{SiF_4} increases the reaction rate, which in turn results in higher reaction temperatures. For a constant weight of sodium and for a fixed reactor geometry, a range of reaction temperatures can be obtained by varying the pressure of the SiF_4 gas in the system. As a result of this temperature variation, we obtained a variety of morphological forms of silicon. In the scanning electron microscope, silicon has been observed in the form of cubes approximately 0.1 mm from corner to corner (Figure 2), in the form of branches about 0.02 mm long (Figure 3) and as a fine powder with some crystalline structure (Figure 4).

This wide range in the silicon particle size led us to perform a systematic study of the effects of the reaction conditions such as P_{SiF_4} and T_{max} on the morphology of silicon powder. A series of 16 experiments was performed under different pressures of SiF_4 gas. In each of these experiments, approximately 5 g of clean sodium was placed in the nickel dish inside the reaction kettle, and the kettle was evacuated. By external heating of the reaction kettle, the temperature of the sodium metal was raised to 250°C , the vacuum line was cut off, and SiF_4 gas was introduced to perform the reaction. In this series of experiments, the pressure of

^{*} Performed in the glass reaction kettle

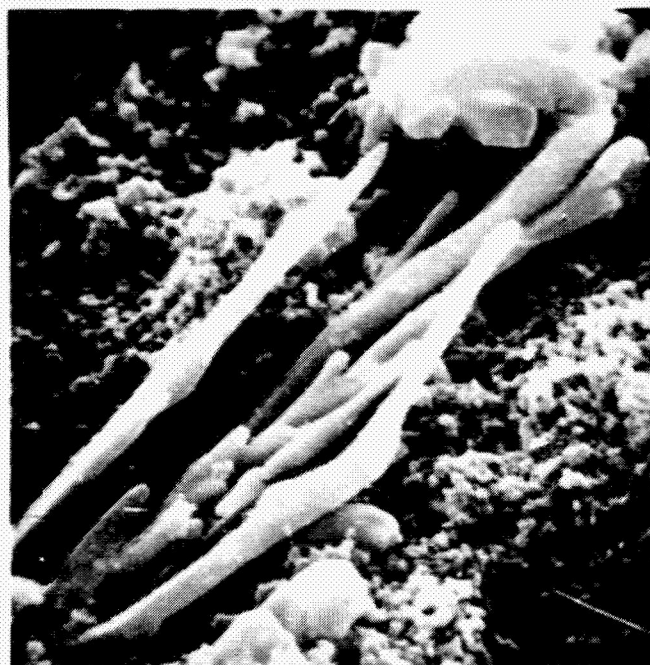
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0.04 mm

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FIGURE 2 SILICON PARTICLE CUBES

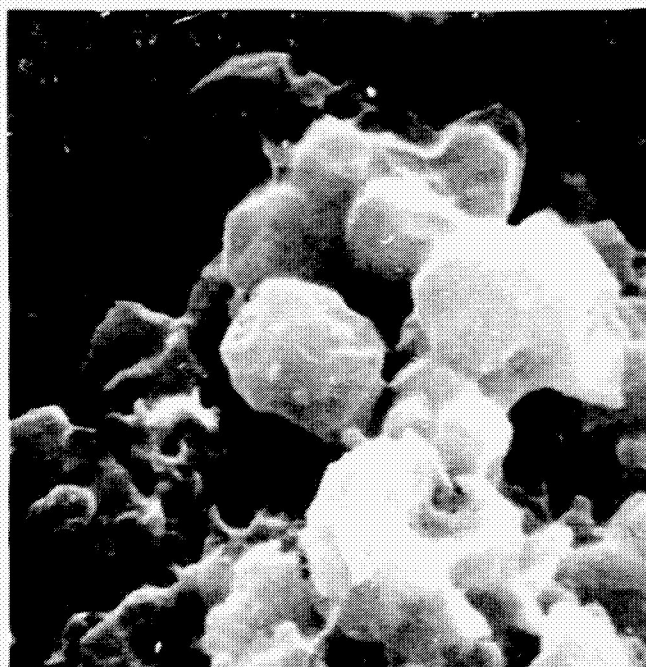


4 μm

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FIGURE 3 SILICON PARTICLE BRANCHES

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2 μm

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FIGURE 4 FINE SILICON POWDER

SiF_4 in the reaction was maintained constant in the range of 0.1 to 1.1 atm. Thus, by fixing the amount of sodium, the total amount of the reaction heat was fixed, whereas adjusting the pressure of SiF_4 in the range of 0.1 to 1.1 atm gave various reaction rates resulting in different reaction temperatures. The reaction temperature in these experiments could not be accurately measured because the thermocouple tip in the reaction zone was quickly coated with an insulating layer of the reaction products. However, estimates of overall average reaction temperature (T_{max}) in different experiments were recorded.

In general, when the P_{SiF_4} was ≥ 1 atm, the estimated reaction temperature was greater than 1400°C . For reactions with $P_{\text{SiF}_4} \approx 0.5$ atm, the estimated reaction temperature varied between 800 and 1100°C , and for $P_{\text{SiF}_4} < 0.5$ atm, the temperature in the reaction system was in the range 600 to 700°C . SEM examination showed the reaction products from a reaction with $P_{\text{SiF}_4} = 1$ atm to be in the form of a hard crust (Figure 5). The energy-dispersive X-ray analysis (EDAX) of the various segments of this crust indicated some silicon segregation from the bulk of sodium fluorides. However, the reaction products obtained under $P_{\text{SiF}_4} = 0.3$ atm appeared to be an easily crumbled mass (Figure 6).

Silicon powders obtained after leaching the sodium fluorides from the reaction products were also examined under SEM. The silicon powder obtained from the reaction performed with $P_{\text{SiF}_4} = 1$ atm had a particle size in the range of 0.2 to 0.5 mm and was crystalline (Figure 7), whereas the silicon powder obtained in the reaction with $P_{\text{SiF}_4} = 0.3$ atm was a fine powder (Figure 8).

These observations suggest that the silicon particle size tends to increase with the P_{SiF_4} and temperature in the reaction system. However, the silicon powder obtained showed a definite distribution of the particle size, which was studied further by sieve analysis, as described in the next section.



1.0 mm

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FIGURE 5 REACTION PRODUCTS OF THE $\text{SiF}_4\text{-Na}$ REACTION
WITH $P_{\text{SiF}_4} = 1.0 \text{ atm}$

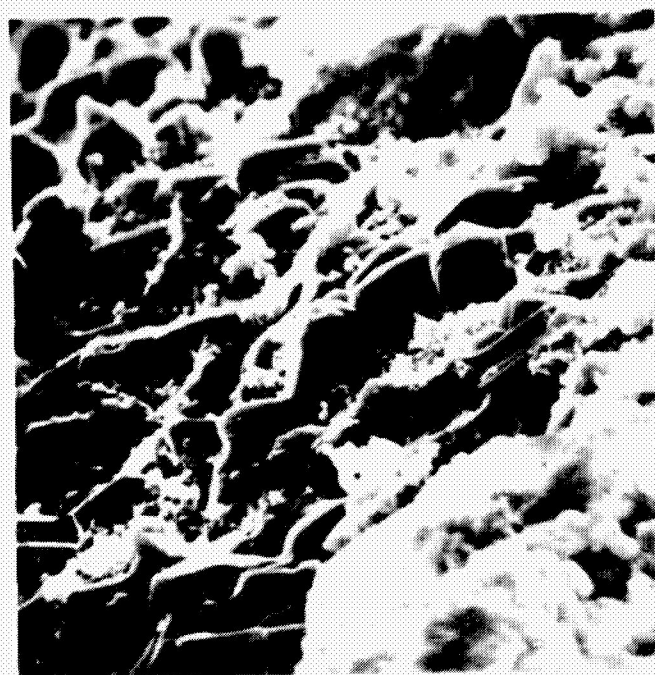
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0.1 mm

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FIGURE 6 REACTION PRODUCTS OF THE $\text{SiF}_4\text{-Na}$ REACTION
WITH $P_{\text{SiF}_4} = 0.3 \text{ atm}$



0.01 mm

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FIGURE 7 SILICON POWDER OBTAINED FROM THE $\text{SiF}_4\text{-Na}$ REACTION WITH $P_{\text{SiF}_4} = 1.0 \text{ atm}$



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FIGURE 8 SILICON POWDER OBTAINED FROM THE SiF_4 -Na
REACTION WITH $P_{\text{SiF}_4} = 0.3 \text{ atm}$

PARTICLE SIZE DISTRIBUTION

To determine the particle size distribution, the leached silicon powders obtained in experiments 2(23.1-23.5) were sieved through a set of standard sieves. The set consisted of five $3\frac{1}{2}$ -inch-diam sieves ASTM No. 20, 40, 60, 100, and 230 mesh, corresponding to sieve openings of 0.841, 0.420, 0.250, 0.149, and 0.063 mm, respectively. For every sample, 0.1 g of dried silicon powder was sieved through this set, and the various fractions were collected and weighed to the nearest ± 0.001 g. The percentage of the total weight retained on each sieve was calculated from these weights. The cumulative weight percentage for five different experiments in the pressure range (55 mm Hg to 700 mm Hg) is plotted in Figure 9. The plot clearly shows that as the P_{SiF_4} increases in the reaction, the percentage of the silicon powder with particle size greater than 250 μm increases. For example, the percentage of the particles with size greater than 250 μm is 45% for $P_{\text{SiF}_4} = 760$ mm, 31% for $P_{\text{SiF}_4} = 750$ mm and about 20% for the range 180-350 mm Hg. This observation again supports the finding that with increasing pressure of SiF_4 in the reaction system (which results in higher T_{max}), the silicon particle size tends to grow larger. We do not yet fully understand the mechanism for this particle size growth.

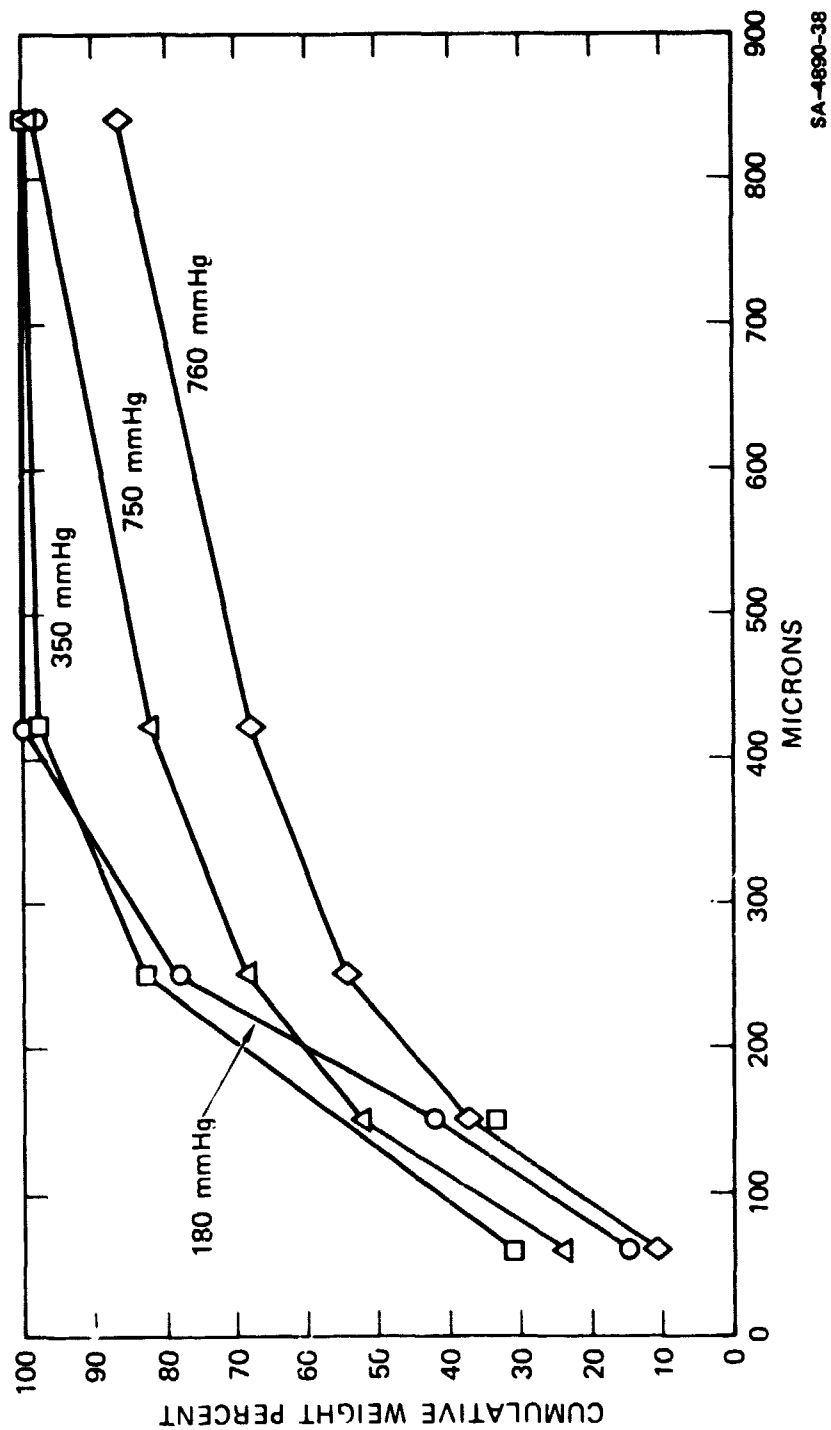


FIGURE 9 CUMULATIVE WEIGHT PERCENTAGE VERSUS THE PARTICLE SIZE OF SILICON POWDER, FOR DIFFERENT PRESSURES OF SiF_4 GAS IN THE SiF_4 -Na REACTION

CHARACTERIZATION OF PRODUCT SILICON

Emission Spectrographic Analysis

We have been analyzing the product silicon routinely by the emission spectrographic method, which gives a semiquantitative analyses of the impurities in silicon. It was quickly realized that most of the impurities of concern in silicon, such as Ti, V, Zr, Cr, Mo, B, P, Al, Na and F, were not being observed, indicating that the amounts of various impurities present in silicon were lower than the detection limit of this method. The level of detection of emission spectrographic method for most of the metals ranges between 10 and 20 ppm wt. However, the estimated detection limit for sodium is 1000 ppm wt and for phosphorus, 4500 ppm wt. Thus, the P and Na content could never be estimated below a few tenths of a percent. Therefore, to determine the impurity content more realistically, we sent a silicon sample for spark source mass spectrometric (SSMS) analysis. The results of this analysis are discussed in a following section.

Melting of Powder Silicon

Before sending the silicon samples for SSMS analysis or making electrical measurements, we melted the powder silicon samples. The silicon powder was first pelletized in a stainless steel die (3/4-inch diameter) under a pressure of 5000 psi. These pellets were placed in a quartz crucible contained in a graphite susceptor. Trace amounts of unleached Na_2SiF_6 in the silicon powder were observed to impede the melting process. The silicon pellets were observed to oxidize along with the etching of the quartz crucible. The mechanism by which the trace amount of Na_2SiF_6 caused the oxidation of silicon pellets is not yet understood.

To solve this problem, we heat-treated the product silicon ($T > 650^\circ\text{C}$) under vacuum for two hours. The Na_2SiF_6 decomposed according to the

reverse of reaction (2). The SiF_4 gas was pumped out, leaving a trace amount of NaF with silicon. The remaining NaF was leached out by another leaching with dilute HCl, resulting in a silicon powder free of sodium fluorides. This powder was repelletized and could be melted by induction heating without any problem.

The molten silicon thus prepared was quenched to prevent impurity segregation and then etched with HF to remove adhering silica. The pieces of clean silicon were sent for SSMS analysis and were also mounted and polished to obtain smooth surfaces for electrical measurements.

Spark Source Mass Spectrometric Analysis

Silicon sample 2(19) was sent to the Instrumental Analysis Division of Commercial Testing and Engineering at Golden, Colorado. The sample was degreased in acetone, then etched with a mixture of HF/HNO₃. It was then rinsed in deionized water, dried under an infrared heat lamp, and mounted in the source of the mass spectrometer. The resulting photoplate was examined for trace elements by the visual "just disappearing" technique versus the silicon M/e 30 isotope line. The results were corrected using the normal silicon/element determined ratio from a variety of other materials. The results are given in Table 1. The concentrations are in ppm wt.

Interesting observations are the low concentrations of doping elements, such as B, Al, Ga, P and As. The concentration of the elements known to be detrimental to solar cells such as Ti(2.0), Zr(2.0), V(0.04), Mn(0.1), and Mo(0.3) are encouragingly low. Also, the low concentrations of Na and F indicate an efficient leaching process used for leaching sodium fluorides. The only impurities present in tens of ppm wt are Fe, Cr, and Ca.

TABLE 1
SPARK SOURCE MASS SPECTROMETRIC ANALYSIS OF
SILICON SAMPLE 2(19)

<u>Element</u>	<u>ppm wt</u>	<u>Element</u>	<u>ppm wt</u>
B	0.1	K	0.01
Al	0.8	Ca	1.0
Ga	0.06	Mg	0.1
P	0.2	Sr	0.2
As	Not observed	Ba	0.1
Zr	0.01	Sc	0.1
V	0.04	Y	0.08
Mn	0.1	Cl	0.08
Mo	0.3	F	0.1
Ti	2.0	C	5.0
Zr	2.0	O	350.0
Ni	2.0	S	0.04
Co	0.5	Cr	11.0
Nb	0.02	Cu	20.0
Na	1.0	Fe	55.0

It is possible that the Fe and Cr impurities were introduced by the liquid sodium contained in the stainless steel container. The source of the copper impurity is not quite clear, although it could have been introduced by the liquid sodium itself because the only two observed impurities in sodium metal used (as per the emission spectrographic analysis) were Cu (8 ppm wt) and Ca (100 ppm wt). It is also suspected that the source of Ti and Zr impurities could be the quartz crucible used for melting silicon.

It must be emphasized here that the silicon sample analyzed was obtained without any purification of SiF_4 gas and sodium metal. It is believed that with purification of the reactants with some corrective measures such as a nickel liner for the sodium container, and using high purity quartz crucibles for silicon melting, the impurity content of silicon can be further reduced.

This silicon material can be purified further either by SiF_2 gas disproportionation or by electrochemical routes, but both methods require further research. This silicon material could be a suitable feedstock for a Czochralski puller, but in that case, silicon will be further purified, because, as is well known, the segregation coefficients of most of the metallic impurities are highly favorable. The analyses reported here are for the silicon samples that were not refined by zone refining Czochralski pulling, or other liquid/solid segregation processes.

Phosphorus Analysis

The phosphorus content in sample 2(19) was determined independently by analyzing the sample with a colorimetric method. The phosphorus content was found to be less than 90 parts per billion, which agreed reasonably well with the SSMS result of 200 ppb.

Electrical Measurements

Samples 2(19) and 2(20) obtained after induction melting of silicon powder were mounted and polished to obtain smooth surfaces of an approximate area of $1 \times 1 \text{ cm}^2$. Resistivity values were measured using a four-point probe of 0.02 inch spacings. These measurements were made on at least five different positions of each sample. The results are given in Table 2. A thermoelectric method was used for typing the bulk material in these samples, and the bulk material in both samples was p-type.

Table 2

ELECTRICAL MEASUREMENTS

<u>Sample No.</u>	<u>Resistivity Ohm Cm</u>
2(19) p-type	0.1 - 0.5
2(20) p-type	0.2 - 0.25

STUDIES IN PROGRESS

We are continuing further investigation of suitable methods for introducing liquid sodium into the reactor. The information obtained from these studies will be utilized for process scale-up.

We are also attempting to pin-point the sources of impurities such as Cr, Cu and Fe so that we may further decrease the impurity content in SRI silicon.

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